PITTSBURGH ATOMIC SCIENCES INSTITUTE

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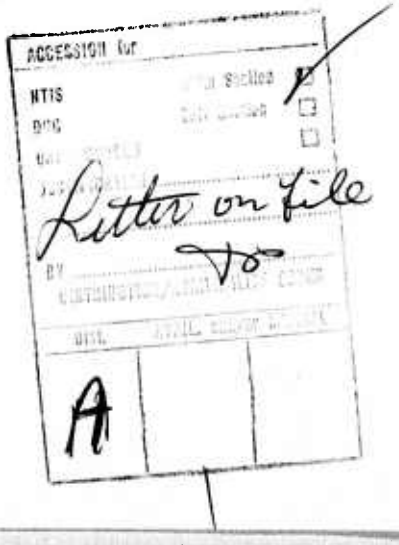

TECHNICAL PROGRESS REPORT NO. 19

Pittsburgh Atomic Sciences Institute

University of Pittsburgh

Pittsburgh, Pennsylvania 15260

I. Summary of Research

The following research projects are identified by title, senior investigator(s) in charge of the work, and the general program to which they belong. This summary only covers advances during the period since our last progress report (dated April 30, 1975).

A. Laser Studies

1. Laser Ion Molecule Reaction Rates (M. A. Biondi)

The detectable wavelength range of the drift tube - mass spectrometer - optical spectrometer apparatus was extended to $\lambda \gtrsim 9000\text{Å}$ in order to determine excited state production and channel branching ratios for the fast, non-resonant charge transfer (NRCT) reaction

$$He^+ + Hg \rightarrow He + Hg^{+*} + \Delta\epsilon(\infty) \quad .$$

It is found that only the $(5d)^{10}\ 7p[^2P_{3/2,1/2}]$ states of Hg^+ are formed; the $^2P_{3/2}$ state involves an exoergic reaction energy defect of $\Delta\epsilon(\infty) = 0.27$ eV, while the $^2P_{1/2}$ state involves a substantially larger defect of 0.72 eV, yet the reaction branching ratio is almost unity, [3/2]:[1/2] = 1.4. Further, no final states having intermediate energy defects are detected. These are $(5d)^9$ 6s 6p states which should exhibit less favorable curve crossings between the He^+ - Hg initial and He - Hg^{+*} final states, leading to small reaction probability. Thus, the origin of the 6149Å and 7944Å lasing transitions is experimentally defined and possible modifications of NRCT theory are indicated.

Studies of the production of N_2^{+*} ($B\ ^2\Sigma_u^+$) states by the fast NRCT reaction

$$He_2^+ + N_2 \rightarrow 2\ He + N_2^{+*}$$

indicate that the final vibrational states of N_2^+ ($B\ ^2\Sigma_u^+$) are populated by vertical transitions within the Franck-Condon region connecting the undistorted potential energy curves of $N_2(v = o)$ and N_2^{+*}.

2. Metal Atom Chemi-Excitation (F. Kaufman, M. A. Biondi)

Further series of experiments were carried out to determine the line width and chemical origin of the sodium D-line chemiluminescence excited by reaction of Na with "active" oxygen downstream of a microwave discharge at about 2 torr pressure. The extinction of the glow upon removal of O-atoms by NO_2 titration even in the continued presence of metastable $O_2(^1\Delta_g)$, the linear dependence of its intensity on O-atom concentration, and the higher order dependence on Na-atom concentration favor a mechanism involving O and Na_2, particularly since very little O_3 is present under these conditions. Two possible reaction paths must be considered:

(1) $O + Na_2 \rightarrow NaO + Na^*$. This requires a higher Na-O bond strength ($\geq$ 2.9 eV) than either the JANAF value (2.8 $\pm$ 0.4 eV) or that reported by Hildenbrand and Murad (2.6 $\pm$ 0.2 eV). Moreover, an additional $\sim$ 0.1 eV of translational energy release is observed corresponding to the broadened Na-lines, which requires that $D_{Na-O} \geq 3.0$ eV.

(2) $O + Na_2 \rightarrow NaO + Na$, followed by $NaO + O \rightarrow O_2 + Na^*$. Here, the difference between the O_2 and NaO bond energies is greater than the D-line excitation energy (2.1 eV), and places an opposite constraint on the magnitude of Na-O bond energy, i.e. $D_{NaO} \leq 2.9$ eV which is consistent with the above published estimates. Although there is no direct, experimental

evidence for or against either mechanism, (2) is slightly preferred on thermochemical grounds.

D-line widths were measured by Fabry-Perot interferometry for the chemiluminescent reaction with O-atoms coming either from discharged O_2 or from discharged N_2 followed by the titration reaction $N + NO \rightarrow N_2 + O$. In both cases the apparent D-line widths were in the 1100 to 1200°K range, but because of the low intensity of the emission, the complex hyperfine structure of the line, and the modest resolution of the interferometer (~ 0.045 cm^{-1}), the uncertainty in the measured width (~ 0.005 cm^{-1}) is fairly large and corresponds to about $\pm$ 200°K for the effective translational temperature of Na^*. Moreover, repeated attempts to measure the line width in fluorescence at 500°K gave results 200 to 300°K too high. Applying such a correction to the active oxygen line widths we obtain a range of 800 to 1000°K for the chemiluminescent Doppler temperature which corresponds to a translational energy release of 0.06 to 0.10 eV. Interferometric observations of the sodium nightglow in the upper atmosphere by Sipler and Biondi have shown Doppler temperatures of 600 $\pm$ 50°K. Considering the $\pm$ 200°K uncertainty of our chemiluminescent emission measurements we can not exclude the possibility of a similar excitation mechanism for both phenomena. This would have to be (2) above, since (1) involves the direct reaction of Na_2, whose atmospheric concentration must be negligibly small. The NaO, which is the likely precursor of the emission, would then be produced by the $Na + O_3$ reaction in the upper atmosphere.

3. <u>Production of Excited States by Dissociative Electron-Ion Recombination and Dissociative Excitation</u> (<u>M. A. Biondi and E. C. Zipf</u>)

Studies of the electron temperature dependence of dissociative recombination of electron with Xe_2^+ ions are in progress which will span energy ranges of interest for laser plasmas. Further, the changing production

of the various excited states with changes in T_e is currently under study in the microwave afterglow - electron heating - optical spectrographic apparatus. Excited states formed by dissociative recombination are clearly distinguishable from those excited by other afterglow processes.

We continue to study the excitation of metastable, pseudo-metastable and Rydberg atoms and molecules by electron impact on a large variety of target gases. In these experiments time-of-flight, quenching and optical techniques are used to measure the absolute excitation cross sections and to explore the details of the dissociation process itself. In recent months we have been concentrating on hydrogen, its isotopes, and compounds and have observed some unusual mass-dependent effects that apparently arise because of a velocity dependent competition between autoionization and predissociation. These studies also show quite clearly the very important role played by doubly excited states in electron-impact induced dissociation.

4. Theoretical Studies - Laser Physics (J. N. Bardsley)

A. Analysis of reaction-rate measurements in drift tubes

In the measurement of the rates for ion-molecule reactions the use of drift tubes has helped to bridge the energy gap between experiments performed in the thermal regime, around 0.03 eV, and beam experiments, which become difficult at energies below 5 eV. In a drift tube one increases the average energy of the ions by the application of an external electric field. However in order to interpret such experiments one needs to know the distribution of energies appropriate to the ions in the drift tube, and experiment measurement of this distribution is extremely difficult. Thus we have performed Monte-Carlo simulations of the ion motion and have constructed histograms of the speed and velocity distributions. Our results have been used in the analysis of reaction rate measurements made in this laboratory and by the aeronomy group at the NOAA laboratory in Boulder.

B. Potential Curves for Alkali Dimers

It has been proposed that the A↔X transition in the alkali dimers might lead to a very efficient laser in the visible region. However there is an uncertainty as to whether the upper levels may be depopulated due to predissociation by a triplet state. There is almost no experimental information regarding the potential curves of the triplet states of the alkali dimers, and indeed for Rb_2 and Cs_2 even the potential curves for the $A\ ^1\Sigma_u$ states are not established. Thus we have applied our pseudopotential program to these systems and have computed the potential curves for five of the states of Na_2, Rb_2 and Cs_2. Our results for Na_2 compare favourably with ab initio calculations, with errors of $\lesssim$ 0.1 eV. For Rb_2 and Cs_2 accurate ab initio calculations have not been performed so that the pseudopotential method offers the best prospect for accurate calculations.

C. Charge transfer at low energies

We have almost completed our investigation of resonant charge transfer and have developed a technique by which we can obtain estimates of the charge transfer cross section for any ion. Our results appear to be consistent with most of the available experimental data at energies around 100 eV. We also have obtained values at lower energies at which reliable experimental information is sparse. The ions we have studied are H^+, He^+, Li^+, Ne^+, Na^+, K^+, Ca^+, Kr^+, Rb^+, Xe^+, Cs^+, U^+, H^-, Na^- and Cs^-. By comparing our results for Kr^+ and Xe^+ with mobility data we have confirmed that measurements of the drift velocity give the most reliable estimates of the charge transfer cross sections at thermal energies.

D. Rotational excitation of diatomic molecules

We have just begun an investigation of resonant rotational excitation of diatomic molecules by electron impact. One of our aims is to assess the importance of this process as a heating mechanism in a CO laser. If as much

as 5% of the electron energy is lost by this means, there could be a significant reduction in the efficiency of the laser.

B. Atmospheric Radiation Backgrounds

5. Particulate Technology (W. L. Fite)

I. Laboratory Experimentation

A. Detection of natural airborne particulates. We have continued to monitor ambient air particulates using a simple surface ionization particulate detector particularly concentrating on ambient variations in detectable particulates, and correlation with other types of particulate and pollution monitors. Night time excursions appear to correlate very well with smokestack clearing, the detectors appear to be much more sensitive to coal fly ash than other materials. Rush hour excursions appear to come from stirring up of dust on the streets, rather than from automboile exhausts. Clean haze does not actuate the detectors.

Recent mass analysis studies of basic negative surface ionization performed in part in this laboratory suggest that negative surface ionization may be able to detect particulates containing nitrates and sulfates.

B. Water droplet effect. Progress on these experiments which seek to determine the extent to which pure water droplets actuate a hot surface that has been treated with embedded alkalis and cause positive ions to be emitted, has progressed slowly due to illness of the graduate student who is doing this work. Nonetheless definite progress has been made. The electrospray device used to generate the droplets and electrically charge them, the Faraday cylinder to detect the charge and the velocity of the charged droplets passing through vacuum seems to be working, and techniques to calibrate the Faraday cylinder for absolute charge on the particulate seem to be working satisfactorily. Given the charge and the velocity, and learning the energy

per unit charge from a deflection in an electrostatic field, one can determine the mass of the droplet. This droplet then strikes the surface and the burst of ions produced is correlated with the mass of the droplet.

Our objective remains to determine whether the water droplet effect can be used in conjunction with a regular alkali-free hot surface to determine whether an aerosol consists of water or ice crystals, or of materials other than water such as are found in common smokes and dusts.

II. Field Experiments

Over the summer the instrument for carrying on a balloon-parachute flight package was completed and fully tested. It is now in Palestine, Texas awaiting flight which is now scheduled for October 16. We continue to be optimistic that its first flight will yield meaningful data on dust in the stratosphere, and give encouragement to further development into a rocket borne package capable of examining meteoritic dusts in the D region of the ionosphere.

C. Infrared Chemiluminescence and Early Warning

6. Infrared Emission from Atom-Molecule and Fuel-Oxidizer Reactions; Vibrational Relaxation (F. Kaufman)

Vibrational chemi-excitation and relaxation processes are studied in our versatile, highly sensitive infrared chemiluminescence apparatus which utilizes background-limited detectors for the 1 to 6 μm wavelength range, cooled circularly variable filters for spectral dispersion, and fast flow reactor configuration. Three projects are presently under active study: (1) Initial, unrelaxed vibrational distributions in simple, exothermic atom-molecule reactions such as $H + Cl_2 \rightarrow HCl^{\ddagger} + Cl$ are being measured experimentally and emission spectra are compared with calculated spectra from a large computer program which takes full account of the known energy levels and transition probabilities of simple product molecules such as HCl

and HF. This program plots out synthetic spectra which correspond to any desired mix of vibrationally excited states, assumes complete rotational relaxation, folds in the experimentally measured spectral resolution (about 0 03 to 0.07 μm for $HCl^{\ddagger}$), adjusts for black body calibration, and compares with experimental data points. For $HCl^{\ddagger}$ produced in the H + Cl_2 reaction, for example, such comparisons have yielded relative populations in states of v = 1 through 5 of 0.50, 1.25, 1.00, 0.25, and 0.03, respectively, in good agreement with published spectra at total pressures which are 4 to 5 orders of magnitude lower than ours. This enables us to study subsequent relaxation processes of all v-states. Low pressure "arrested relaxation" experiments are unable to provide such information.

(2) Vibrational relaxation experiments, especially of high v-states, are now being started. They are particularly important in HCl, DCl, HF, or DF laser applications where little information is now available on such relaxation processes. The experimental method is very simple: Unrelaxed distributions are generated by suitable atom-molecule reactions; potential quenching molecules are added either at varying concentrations from a fixed inlet or at constant concentration from an axially movable injector tube; and intensities of specific spectral features characteristic of certain v-states are monitored as function of the added quencher. Preliminary experiments on $OH^{\ddagger}$ relaxation were carried out where $OH^{\ddagger}$ in v = 1, 2, and 3 was produced by the H + NO_2 reaction. Excess NO_2 was added and its quenching rate constant, k_Q, was measured approximately for v = 1 and 3 with the result that $k_Q = 3 \times 10^{-12}$ cm^3 sec^{-1} for v = 1 and 9×10^{-12} for v = 3. For $HCl^{\ddagger}$ in v = 4, a few qualitative experiments suggested very rapid relaxation by Cl_2 with k_Q in excess of 10^{-11} cm^3 sec^{-1}. Detailed, systematic relaxation studies of HCl and HF will now be carried out.

(3) Some fuel-oxidizer emission spectra were recorded for the reaction of O-atoms with monomethyl hydrazine at total pressures of about 1.5 torr and with 0.4 mtorr of monomethyl hydrazine and 1.5 mtorr of atomic oxygen. In addition to strong OH fundamental and overtone bands, intense emission was observed at 3.8 and 1.9 μm which has not yet been fully characterized.

II. Publications and Technical Presentations

A. Publications

Calculations of Ion-Atom Interactions Relating to Resonant Charge-Transfer Collisions, J. N. Bardsley, Phys. Rev. A11, 1911, 1975.

Computation of Speed Distributions for Ions in Drift Tubes, J. N. Bardsley, to be published, J. Phys. B.

Pseudopotential Calculations for Na_2^+, Na_2 and Na_2^-, J. N. Bardsley, submitted to Chem. Phys. Lett.

Electron-Positron Pair Bound to an Extended Dipole, J. N. Bardsley, submitted to Phys. Rev. B.

An Automatic Real-Time Detector and Sizer for Submicron Airborne Particulate Matter, W. L. Fite, R. L. Myers, T. M. Barlak, to be published in Rev. of Sci. Instr., 1975

A New Computer Controlled Quadrupole Mass Spectrometer System, W. L. Fite, M. A. Hender, and R. L. Myers and Y. P. Chong, to be published.

Submicron and Centimicron Particulate Detection Using Surface Ionization, W. L. Fite and R. L. Myers, to be published in American Laboratory Magazine, 1975.

Kinetics of the Reaction $OH + HNO_3 \rightarrow H_2O + NO_3$, J. J. Margitan, F. Kaufman and J. G. Anderson, Int. J. Chem. Kin., Symposium 1, 281, 1975.

Hydrogen Chemistry: Perspective on Experiment and Theory, F. Kaufman, in "Atmospheres of the Earth and the Planets", B. M. McCormac Ed., D. Reidel Publishing Company, Dordrecht, Holland, p. 219 (1975).

Gas Phase Hydrogen Atom Recombination, L. P. Walkauskas and F. Kaufman, 15th International Combustion Symposium, The Combustion Institute, 1975, p. 691.

Re-evaluation of the BEBO Method, R. M. Jordan and F. Kaufman, J. Chem. Phys. 63, 1691 (1975).

Kinetics of the Reaction $OH + D \rightarrow OD + H$, J. J. Margitan and F. Kaufman, Chem. Phys. Letters, 34, 485, 1975.

Dissociation of CH_4 and CD_4 by Electron Impact: Production of Metastable and High-Rydberg Hydrogen and Carbon Fragments, B. L. Carnahan, T. F. Finn, W. C. Wells, and E. C. Zipf, J. Chem. Phys. 63, 1596, 1975.

On the Dissociative Excitation of Rydberg Atoms by Electron Impact. I: N_2, W. C. Wells, W. L. Borst, and E. C. Zipf, submitted to the Physical Review, 1975.

On the Dissociative Excitation of Rydberg Atoms by Electron Impact. II: CO_2, W. C. Wells, W. L. Borst, and E. C. Zipf, submitted to the Physical Review, 1975.

The Dissociative Excitation of H_2, HD, and D_2 by Electron Impact, B. L. Carnahan and E. C. Zipf, submitted to Physical Review Letters, 1975.

B. Technical Presentations

Theory of Low-Energy Electron-Atom Collisions and Related Processes, J. N. Bardsley, 9th Int'l. Conference on the Physics of Electronic and Atomic Collisions, Seattle, July 1975.

Charge Transfer Cross Sections for Rb^+-Rb, Cs^+-Cs and U^+-U at Low Energies, J. N. Bardsley and S. Sinha, 9th ICPEAC, Seattle, July 1975.

OAST Review of Program in Atomic and Molecular Physics, W. L. Fite, technical talk, Headquarters, NASA.

Associative Ionization, W. L. Fite, American Society of Mass Spectrometry Meeting, Houston, Texas, May 27, 1975.

Secondary Processes Involving Associative Ionization of Uranium Atoms, W. L. Fite, contributed paper IXth ICPEAC Meeting, Seattle, Washington, July 24-30, 1975.

Studies of Positive and Negative Ion Associative Ionization in Crossed Beams of Uranium and N_2O, SF_6, Br_2, H_2O, CHF_3 and O_2, contributed paper IXth ICPEAC Meeting, W. L. Fite, Seattle, Washington, July 24-30, 1975.

Associative Ionization, W. L. Fite, invited contribution, 3rd IUPAC Symposium on Plasma Chemistry, Rome, Italy, September 18, 1975.

Associative Ionization, W. L. Fite, lecture at the Max Planck Institut fur Stromungsforschung, Gottingen, Germany, September 29, 1975.

Reactions of Ions Formed by Associative Ionization, W. L. Fite, talk given at the Ecole Polytechnique Palaiseau, Paris, France, October 2, 1975.

Kinetics of Some Stratospheric Reactions of Chlorine Species, F. Kaufman, invited paper at 169th National Meeting, American Chemical Society, Philadelphia, Pa., April 9, 1975.

Stratospheric Chemistry, the SST, and Kinetics of some OH Reactions, F. Kaufman, seminar at Temple University, Philadelphia, Pa., May 1, 1975.

Stratospheric Chemistry and Kinetics of OH- and Cl-Reactions, F. Kaufman, seminar at NASA Lewis Research Center, Cleveland, Ohio, May 12, 1975.

Energy Spectra of Long-Lived Excited Nitrogen Atoms Produced by Electron-Impact Dissociation of N_2, 9th ICPEAC, Seattle, Washington, 1975, W. C. Wells, W. L. Borst, and E. C. Zipf.

C. Other Activities Relating to ARPA

In August 1975 J. N. Bardsley visited the Lawrence Livermore Laboratory and Los Alomos Scientific Laboratory for consultations regarding laser isotope separation schemes and several reactions relevant to laser development.

F. Kaufman attended an Executive Committee meeting of the Division of Chemical Physics of the American Physical Society in Denver, Colorado, on April 1, 1975.

F. Kaufman attended meetings of the Atmospheric Chemistry Panel of the Climatic Impact Committee of the National Academy of Sciences on April 9 and 10 in Philadelphia, May 18 and 19 in Washington, D. C. and a summer study at Snowmass near Aspen July 20 to 26. He also attended a meeting of the Climatic Impact Committee in Washington, D. C. on September 20 and 21.

M. A. Biondi and F. Kaufman met with Dr. Peter Clark at ARPA for discussions of the laser program at Arlington, Virginia on April 30, 1975.

F. Kaufman attended a preflight simulation meeting of the Ultraviolet Absorption Experiment of the Apollo-Soyuz Test Project at Houston, Texas on April 24 and took part in the ground control of the experiment at the Johnson Space Flight Center on July 18 and 19.

F. Kaufman took part in a workshop on the stratosphere at the Goddard Space Flight Center as working-group chairman for laboratory measurements on May 28 to 30 and agreed to serve on the NASA Stratospheric Research Advisory Committee whose first meeting was held in Washington, D. C. on July 31 and August 1, 1975.

F. Kaufman attended the first meeting of the Advisory Board of the Office of Chemistry and Chemical Technology of the National Academy of Sciences in Chicago, Illinois on August 28, 1975.

E. C. Zipf launched a Nike Apache rocket into the Equatorial anomaly above Lima, Peru as part of Project Antiquari (June, 1975).

E. C. Zipf launched a Nike Hawk rocket from Wallops Island, Va. during September, 1975 to study the photoelectron energy spectrum of the day airglow.

E. C. Zipf attended the preliminary planning meetings for a series of auroral rocket experiments to be conducted from Fort Churchill this winter.

III. Visiting Scientists

Y. Demkov, Leningrad State University

A. Ek, Allegheny County Air Pollution Control, Department of Health

W. J. Lassiter, NASA Langley, Hampton, Virginia

C. Linberger, University of Colorado

J. P. Toennies, Director, Max Planck Institut fur Stromungsforschung, Gottingen, Germany

IV. Degrees Awarded

Y. P. Chong, Ph.D., September 1975

Senior Investigator	Est. Funds Expended and Committed (Thousands)
J. N. Bardsley	1.8
M. A. Biondi	8.2
W. L. Fite	4.2
F. Kaufman	7.7
E. C. Zipf	3.2
Total Expended and Committed	25.1
Available Funds	140.0
Estimated Funds Remaining as of 9/30/75	114.9

University Accounting of Funds	
Expended as of 9/30/75	16.1
Available Funds	140.0
Remaining Funds as of 9/30/75	123.9